Study of Chemical Absorption and Swelling Kinetics at 50°C for Polyurethane/ Montmorillonite Clay Nanocomposites

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Abstract– **Layered silicate composites having polyurethane matrix were prepared by in situ polymerization. Montmorillonite clay was pretreated with centyl tri-methyl ammonium bromide (CTAB) to convert hydrophilic clay into organophilic MMT so that it is compatible with hydrophobic polyurethane matrix. The composites so prepared were characterized for their morphology using SEM and chemical absorption in various chemicals like toluene, ethyl acetate, xylene, hexane, methanol, DMF, tetrahydrofuran, acetone, petroleum ether, distilled water, saline water, and ethanol with varying solubility parameters. The absorption study revealed that depending upon the absorption the solvent can be divided into three categories, high absorbing, medium absorbing and low absorbing depending upon their solubility parameters vis-a-vis polyurethane resin. Two high absorbing solvents i.e. ethyl acetate and xylene, one medium absorbing i.e. ethanol and one low absorbing i.e. saline water were taken to further study the swelling kinetics at 50oC to establish its barrier properties and diffusivity. For all the solvents, the presence of montmorillonite layers caused a decrease in permeability due to more tortuous path for diffusing molecules that must bypass impermeable platelets.**

Keywords– **Chemical absorption, Montmorillonite clay, Polyurethane, nanocomposite, swelling kinetics.**

I. INTRODUCTION

Nanocomposites are new class of materials with improved physical, thermal, mechanical and barrier properties than those of conventional composites due to the much stronger interfacial forces between the dispersed nanometer-sized domains and the matrices. Clay/polymer nanocomposites offer tremendous improvement in a wide range of physical and engineering properties for polymers with low filler loading. The major development in this field has been carried out over the last one and half decades. The significant progress has been made in the development of synthetic methods, applications to engineering polymers, and the investigation of major engineering properties.

Natural clays are composed of oxide layers with cations in between layers. These layered materials are present in the form of the aggregate with a size of about 0.1–10 mm consisting of several primary particles with a height of about 8–10 nm. The primary particles are composed of a number of layers, and the thickness of the layers is about 0.96– 1.0 nm .

Nanoscale layered clays with very high aspect ratios and high strength can play an important role in forming effective polymer nanocomposites owing to their intercalation chemistry. Montmorillonite has been particularly important in polymer nanocomposites. Montmorillonite is a crystalline, 2:1 layered clay mineral in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets.

Due to the poor compatibility of MMT with organic monomers and polymer matrices, it is necessary to modify MMT in the preparation of polymer–MMT nanocomposites for high performance. An effective way to modify the nature of MMT is to substitute the cations in the interlayer galleries of layers with cationic-organic surfactants. On one hand, organic modifiers can impart hydrophilic properties to the MMT, which can improve the compatibility of MMT with polymers. On the other hand, the gallery spacing of the modified MMT becomes larger than that of MMT. Organically modified clays play an important role in the formation of the structure and morphology of polymer/clay nanocomposites, and thus significantly influences material properties. Therefore, the choice of modifiers used to treat clay is crucial to prepare polymer/clay nanocomposites with enhanced properties. At present, alkylammonium and alkylphosphonium are used widely to treat MMT . In the present study we have used centyl tri-methyl ammonium bromide (CTAB) for converting the hydrophilic clay into hydrophobic form.

Tien and Wei synthesized PU/MMT nanocomposites from PPG, MDI and DMF in order to induce efficient exfoliation and dispersion of MMT layers in the PU matrix. It has been reported that nanoclay can increase the hardness and scratch resistance. Nanosilica has enhanced the tensile strength and elongation of polyurethane elastomers, however the modulus and hardness are lower than those of the corresponding micro size filled polyurethane, because the surface properties, particle size, and dispersion of nano particles are diversified. However, studies on swelling kinetics for these composites in the solvents like ethanol, methanol, saline water, petroleum ether, ethyl acetate and hexane has not been reported anywhere.

The interaction between the organic solvents and polymer membranes have been studied for almost half a century; nevertheless a complete understanding of the transport mechanism, namely, sorption, diffusion, and permeation, at the molecular level is still not well understood. The interest in the accumulation of a large body of coherent and accurate experimental data on diffusion coefficient (D), permeability coefficient (P), and sorption coefficient (S), of solvents molecules through polymer membranes is attributed to a number of important engineering applications that depend wholly or partly on such phenomena. These include protective coatings, paints, and varnishes, electronic devices and cable sheathing materials, packaging goods for food and beverages, selective barriers for the separation of liquid mixtures, biomedical devices etc.

In view of the importance of polyurethane nanocomposite as a membrane in engineering applications, we found it necessary to explore the interactions with several organic solvents. In this, we will present some useful engineering data on sorption, diffusivity, and permeability of a number of organic and inorganic solvents, which have some relevance in industry and engineering.

II EXPERIMENTATION

A. Materials

Polypropylene glycol (PPG), Montmorillonite K-10 was supplied by Fluka. Centyl tri-methyl ammonium bromide (CTAB) was supplied by National Chemicals, India. Dimethyl formamide (DMF) was procured from E-Merck, xylene, ethyl acetate were procured from Qualigens, India.

B. Modification of Montmorillonite K10

To disperse montmorillonite in a polyurethane matrix, it was necessary to first replace the hydrophilic inorganic exchange cations with more alkyl ammonium ions. To achieve this, 12.04 gram of Na montmorillonite was added to 500 ml of the aqueous solution of CTAB (0.5 wt %). The suspension was vigorously stirred for 4 hours at 60°C. A white solid product formed after filtration was collected and repeatedly washed by distilled water and acetone. After removal of the solvent by evaporation under reduced pressure, the solid product was dried in a vacuum oven at 70°C for 10 hrs. The obtained organophilic montmorillonite was ground and screened with sieve.

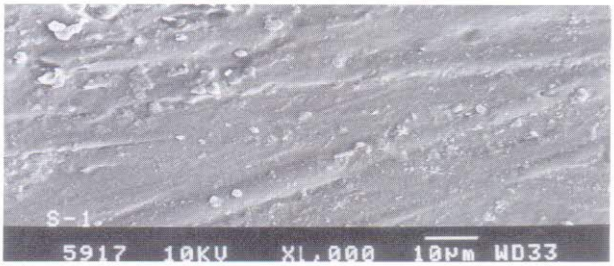

Fig. 1 SEM of polyurethane nanocomposite samples containing 2 wt% of nanoclay

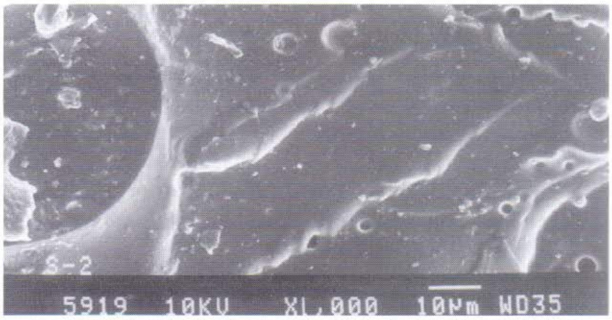

Fig. 2 SEM of polyurethane nanocomposite samples containing 1 wt% nanoclay

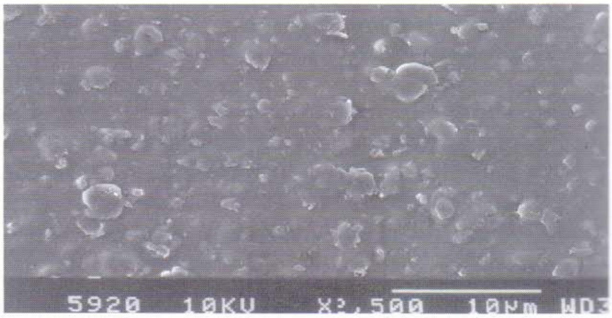

Fig. 3 SEM of polyurethane nanocomposite samples containing 10 wt% nanoclay

C. Synthesis of polyurethane resin

PU was prepared using dehydrated PPG, MDI and DMF solvent. The reaction was carried out in a well agitated reaction vessel maintained at a constant temperature of 80°C. When the reaction mass become very viscous but had flow characteristics, the reaction mass was poured into the mold and the necessary pressure was applied for sheet forming. Nanocomposite of polyurethane/montmorillonite was prepared by in-situ polymerization using same method in presence treated organoclay. The percentage of clay was varied by weight of the total mixture i.e.1%,2%,4%,6%,8% and 10%. Continuous stirring and mixing under nitrogen atmosphere led to increase in viscosity of the reaction mixture which when had appropriate flow was poured on the mold and kept under pressure and room temperature overnight. The sheets were then cured at room temperature for few days.

D. Characterization

Morphology

Scanning electron micrographs were obtained on a JSM 6100 CX (JEOL) electron microscope. The sample preparation technique used was based on Kato's osmium tetraoxide staining technique and Matsuo's two step sectioning method. The SEM of the composite samples was done to observe the dispersion of clay in the composite.

Chemical Absorption

To test resistance of nanoclay polyurethane composites towards various chemicals, they were dipped in various organic and inorganic solvents. Samples of almost equal sizes were cut from a particular sheet, weighed accurately and then immersed in a solvent in numbered beakers for 48 hours. These samples were then withdrawn, wiped with a tissue paper to remove excess solvent and then weighed again. The surface conditions were also noted. The percentage absorption was calculated using equation (1), (9).

$$A = \frac{m_t - m_i}{m_i} \times 100 \qquad (1)$$

Where, m_t is the mass of sample at time "t" (48 hours in this case), mi is the dry weight of sample. The samples were examined on the basis of physical appearance such as discoloration, loss of gloss, and change in weight. Table 1 presents various solvents with their solubility parameters used for chemical absorption studies.

Swelling Behavior

Polyurethane and its nanocomposite are known to exhibit unique mechanical properties, primarily as a result of two phase morphology. In view of the importance of polyurethane, as barrier material, in several engineering areas, it is important to know its transport characteristics with respect to common solvents. To study the swelling kinetics, the so-called pat-and-technique was used for liquid sorption 10. Square samples (size 25 x 25 mm) of definite thickness, after taking the dry weight were placed in different solvents in a standard joint test tube, which was maintained at a constant temperature of 50±0.1 °C (Julabo, VC-5,with cooling a well as heating arrangement). Specimens were taken out at regular intervals or time; solvent adhering to the surface was rubbed off, weighed immediately and replaced in the solvent. This procedure was continued till equilibrium swelling was achieved. This was repeated for specimens with different styrene content ensuring the reproducibility of results. The time taken for wiping out the solvent from sample surface and weighing was kept small in order to minimize the error due to solvent evaporation.

III RESULTS AND EXPERIMENTS

A. Morphology

The figures 1 to 3 show the scanning electron micrographs of polyurethane clay nanocomposites. Figure 1 shows even micrographs containing 1 % clay, figure 2 of 2% clay and figure 3 shows nanocomposite containing 10% clay. It is evident from these figures that distribution of clay is quite uniform, especially in figure containing 10% clay, also there is a good adhesion between clay and polymer which is indicated in the barrier properties in the following sections. Tactoids of clay can be seen in all the figures indicating intercalated nanocomposites. Tactoid size ranges from 0.2 to 1 μm.

1) Chemical Absorption

Chemical absorption in various organic and inorganic solvents i.e. toluene, ethyl acetate, xylene, hexane, methanol, DMF, tetrahydrofuran (THF), acetone, petroleum ether, distilled water, saline water, and ethanol was determined and the results of chemical absorption are given in Table 1. Figure 4 shows the graphical representation of the percentage absorption value for neat polyurethane samples.

It is evident from the results that the DMF, and tetrahydrofuran had the most significant effect on the nanocomposite samples as it affects the whole nature of the sample. The nanocomposites were stable and almost no significance of any of the nanocomposites in solvents like distilled water, acetone, saline water, but the samples became brittle and lost their gloss in solvents like xylene, methanol, ethyl acetate, hexane, toluene, ethanol and petroleum ether. This embitterment was only physical but no soluble fraction was observed. Here the two phases are separated without dissolution and the sheet loses elasticity.

Also it is observed from the result that the percentage absorption is maximum in DMF i.e. it varies from 132% to 173% and also in toluene it varies from 108% to 153%. It was followed by ethyl acetate, xylene, hexane, tetrahydrofuran, and then acetone. If the value of solubility parameters of these solvents is observed, the solvents with solubility parameter close to polyurethane show maximum absorption. The solubility parameter of polyurethane lies between 8 to 11 $(\mathrm{cal/cm^3})^{1/2}$11 . Figure 5 represents variation of absorption with solubility parameter of solvents. It can be observed in the figure that the absorption of solvents is maximum in the solvents within solubility range of 8-12 $(\mathrm{cal/cm^3})^{1/2}$ i.e. the solvents with solubility parameters closest to that of polyurethane.

TABLE 1 PERCENTAGE OF VARIOUS CHEMICALS ON DIFFERENT ABSORPTION POLYURETHANE NANOCOMPOSITE SAMPLES PREPARED.

Solvent used	Solubility parameters (cal/cm3) 1/2	Percentage Absorption						
		Neat	**1%**	**2%**	**4%**	**6%**	**8%**	**10%**
Ethyl acetate	9.10	113.2	135.7	136.8	140.4	143.5	144.18	150.5
Toluene	8.91	108.6	129.4	137.3	143.2	150.1	152.1	153.4
Xylene	8.85	97.1	108.6	109.6	111.3	118.8	119.4	119.2
DMF	12.14	132.1	159.0	163.2	167.0	171.2	172.6	173.3
Tetrahydrofuran	9.52	116.1	130.6	132.9	134.8	135.3	137.2	138.5
Acetone	9.77	84.2	99.4	102.4	103.5	135.3	136.1	138.0
Petroleum ether	--	9.7	15.7	20.5	21.3	26.3	27.9	22.4
Ethanol	12.92	7.9	11.2	15.3	17.0	20.5	23.8	25.0
Hexane	7.24	9.8	17.4	18.0	19.1	18.6	20.6	21.5
Methanol	14.28	12.8	18.9	19.1	20.8	21.6	22.1	23.6
Distilled water	23.5	0.4	0.8	0.82	1.01	1.9	2.35	2.4
Saline water	23.5	0.44	0.54	0.68	1.3	1.67	1.7	2.29

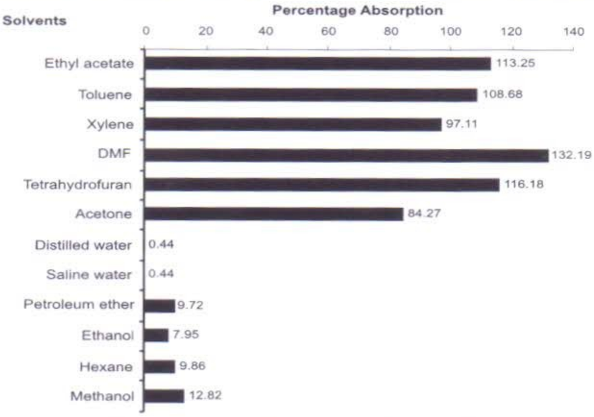

Fig. 4 Percentage Chemical Absorption of Various Chemicals in Polyurethane Sheets

It is evident from the results that the percentage goes on increasing as the nanoclay content increases i.e. the % absorption is minimum for the neat polymer sheet and it increases gradually with the increasing percentage of clay in the polymer matrix 12.

The absorption study has also revealed that depending upon the absorption the solvent can be divided into three types, high absorbing, medium absorbing and low absorbing. These solvents also are classified according to solubility parameters. High absorbing solvents are those with δ equal to that of polymer, medium absorbing are δ close to that of polymer and low absorbing are with δ value deviating from that of polymer. Two high absorbing solvents i.e. ethyl acetate (δ=9.10**(cal/cm^3)$^{1/2}$**) and xylene (δ=8.85**(cal/cm^3)$^{1/2}$**), one medium absorbing i.e. ethanol (δ=12.92**(cal/cm^3)$^{1/2}$**) and one low absorbing i.e. saline water (δ=23.5**(cal/cm^3)$^{1/2}$**) were taken to further study the swelling kinetics at 50°C.

2) *Swelling Kinetics*

The sorption of penetrant species into polymer matrix is quantified in terms of mole percent uptake of solvent (Qt) which was calculated at each time interval using the equation 2 [13-14].

$$Q_t = \frac{m_e / m_r}{m_i} \times 10 \qquad (2)$$

Where, *me* is the mass of solvent taken up at equilibrium, m_r is the relative molecular mass of the solvent and m_i is the dry weight of sample.

At equilibrium, Qt is considered to be Q∞, mole percent uptake of solvent at infinite time. The experiments were performed at 50°C in a controlled water bath. The sorption curves of nanocomposite with varying nanoclay contents, obtained by plotting Qt vs. (time)$^{1/2}$ for ethyl acetate at 50°C are given in figure 6.

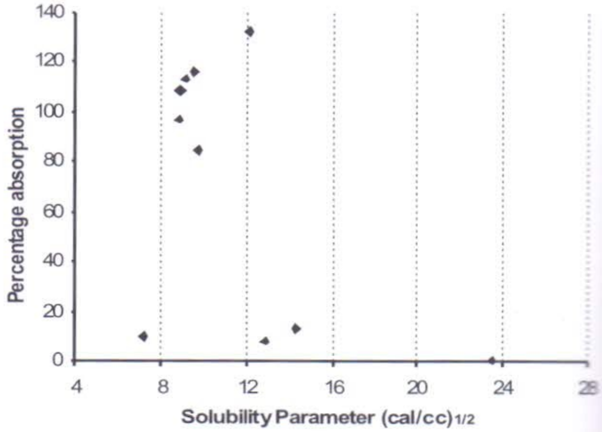

Fig. 5 Figure showing variation of percentage absorption with solvents with different solubility parameters.

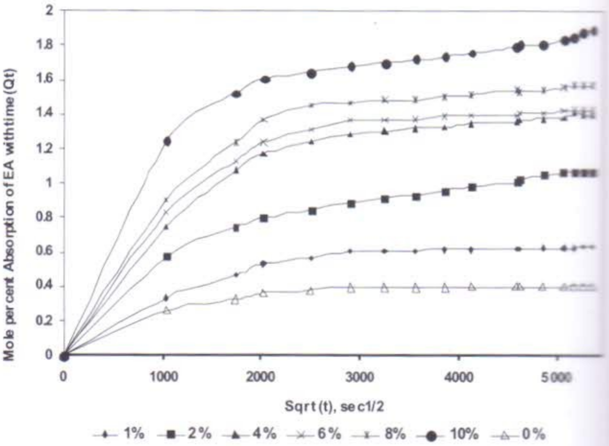

Fig. 6 Variation of mole percent uptake of solvent (Qt) with respect to t1/2 for Ethyl acetate at 50°C

To understand the mechanism of sorption, the values of Qt and Q∞ were substituted in the general equation 3 for transport phenomena.

$$\frac{Q_t}{Q\infty} = Kt^n \qquad (3)$$

Where, Qt is the mole percent uptake at time t, Q∞, is the equilibrium mole percent uptake, k is a constant, which depends on the structural characteristics of the polymer and its interaction with solvent. The values of n determine the mode of transport.

In the equation 3 for transport phenomenon, if n=0.5 diffusion obeys Fick's law, which occurs when segmental mobility of the polymer chains is faster than the rate of diffusion of penetrating molecules. When n=1, the diffusion is said to be non- Fickian (15). For our system, the values of k and n were obtained from the linear plot of ln Qt/Q∞ versus ln t, and are represented in table 2. The values of k, which depend on the structural characteristics of the polymer and its interaction with solvent, are also furnished in the same tables.

The transport of penetrating molecules through polymers is also quantified by other terms such as diffusion coefficient (D) and sorption coefficient (S). The diffusion coefficient, which is a measure of the ability of the penetrating molecules to move among the polymer segment and the sorption coefficient S, which gives an idea about the equilibrium sorption, were calculated from the equation 4 and equation 5.

$$D = \pi \left(\frac{h\theta}{4Q_{\infty}} \right)^2 \qquad (4)$$

$$S = \frac{m_{\infty}}{m_p} \qquad (5)$$

Where, h is the thickness of the sample, is the slope of the linear portion of the sorption curve, m∞ represents the mass of the solvent taken up at the equilibrium and mp represents the initial mass of the sample. The permeability coefficient (P), which gives a combined effect of both D and S, was also calculated using the equation P = D S. The values of D, S and P for the system are summarized in table 2.

The tortuosity factor ( ), is defined as the ratio of the actual distance that a penetrant must travel to the shortest distance that it would have traveled in the absence of layered silicate. As the tortuosity increases the permeability of a composite sample decreases (12). The permeability of polymers with respect to given per-meant depends on both the translational diffusion (D) and solubility constant (S). As well known, D increases with temperature and with strength of attractive interaction between the polymer and per-meant. Permeability decreases with increase in the size of the permeant and with decrease in free volume of the polymer. Polymers that interact strongly with permeants will favor permeability and, conversely, polymers interacting poorly with a given permeant will decrease permeation and thus enhance the barrier properties of composite.

The mass transport mechanism in a nanoplatelet reinforced polymer similar to that in a semi crystalline polymer. The crystallites effect the diffusion process in two ways. They act as impermeable barriers to the gas molecules, forcing them to follow longer paths (16).

In most theoretical treatise the nanocomposite is considered to consist of a permeable phase (polymer matrix) in which non-permeable nanoplatelets are dispersed. There are three main factors that influence the permeability of a nanocomposite: the volume fraction of the nanoplatelets; their orientation relative to the diffusion direction; and their aspect ratio. It is generally accepted that the transport mechanism within the polymer matrix follows Fick's law, and that the matrix maintains the same properties and characteristics as the neat polymer.

Table 2 Values of Diffusivity Coefficient D, Sorption Coefficient S, and Permeability Coefficient P, Slope (n) for the Sorption Curve of Ethyl Acetate at 50 °C for Different Polyurethane Nanocomposite Samples.

Clay %	**D x 10^4 cm^2/sec**	**Ethyl Acetate**				
		S g/g	**P * 10^8 cm^2/sec**	**n ($sec^{-1/2}$)**	**k**	**Q∞**
Neat Resin	14.79	0.52	7.69	0.112	0.15	0.408
1	12.4	0.56	6.94	0.16	0.066	0.637
2	5.39	0.945	5.09	0.178	0.051	1.074
4	2.55	1.234	3.15	0.161	0.091	1.403
6	1.61	1.26	2.03	0.132	0.153	1.433
8	1.43	1.38	1.97	0.134	0.162	1.570
10	0.56	1.667	0.93	0.106	0.301	1.890

Therefore, a decrease of the solubility is expected in the nanocomposite due to the reduced polymer matrix volume, as well as a decrease in diffusion due to a more tortuous path for the diffusing molecules.

Indeed, the volume fraction of nanoplatelets is low and, thus, the reduction of the matrix volume is small. The major factor, then, is the tortuosity, which is connected directly to the shape and the degree of dispersion of the nanoplatelets. The degree of dispersion of the nanoplatelets is determined by the degree of delamination of the clay. The fully delaminated (exfoliated) nanocomposite presents much higher values for the tortuosity factor and the aspect ratio in comparison with the partially delaminated (intercalated) nanocomposite and it is much more effective to be used in barrier membranes.

For all the solvents in the study, the presence of montmorillonite layers cause a decrease in diffusivity and permeability due to more tortuous path for diffusing molecules that must bypass impermeable platelets. As the percentage clay increases the tortuosity increases the length of penetration path for the solvent causing a decrease in diffusivity and permeability. These results are in coherence with the literature (12).

IV. CONCLUSIONS

The following conclusions have been drawn:

1. The scanning electron micrographs of polyurethane MMT clay nanocomposites show good dispersion of clay throughout the matrix.
2. The results of chemical absorption revealed that the DMF, and tetrahydrofuran had the most significant effect on the nanocomposite samples as it affects the whole nature of the sample because solubility parameter (δ) of these solvents is close to that of polymer. The nanocomposites were stable and almost no significance of any of the nanocomposite in solvents like distilled water, acetone, saline water, petroleum ether, but the samples became brittle and lost their gloss in solvents like xylene, methanol, ethyl acetate, hexane, toluene , ethanol and petroleum ether.
3. The absorption study has also revealed that depending upon the absorption the solvent and their solubility parameters, they can be divided into three types, high absorbing ($\delta_{solvent}=\delta_{polymer}$), medium absorbing ($\delta_{solvent}\approx\delta_{polymer}$) and low absorbing ($\delta_{solvent}\neq\delta_{polymer}$). Two high absorbing solvents i.e. ethyl acetate and xylene, one medium absorbing i.e. ethanol and one low absorbing i.e. saline water were taken to further study the swelling kinetics at 50°C.
4. The inclusion of small volume fractions of nanoclay particles in PU matrix decreases their diffusivity and permeability with the increasing content of nanoclay. This can be attributed to impermeability of the inorganic nanoparticles and the tortuous pathway the solvent molecules have to cover during their random molecular motion in order to penetrate the composite.

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