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Water Absorption Properties and Morphology of Polypropylene/ Polycarbonate/Polypropylene-graft-Maleic Anhydride Blends

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ABSTRACT

This study investigates the effect of blending polycarbonate (PC) into polypropylene (PP) matrix polymer on water absorption properties and morphology. The blends, containing 5-35% of polycarbonate and 5% compatibilizer, were compounded using twin - screw extruder and fabricated into standard tests samples using compression molding. The compatibilizer used was polypropylene-graft-maleic anhydride (PP-g-MA). In water absorption test, specimens were immersed in distilled water at 23 and 100°C. In 23°C immersion, PC showed the highest absorption at 0.362 wt.% while PP was the lowest at 0.064 wt.%. The blends demonstrated transitional absorption value between PP and PC. In 100°C immersion, 90/5/5, 80/15/5 and 70/25/5 compositions (PP/PC/PP-g-MA) exhibited lower absorption than PP, indicating enhanced long-term degradation resistance in water compared to PP. Microscopy analysis showed that PC existed as fibers, dispersed throughout PP matrix.

Key words: Polymer blend, polypropylene, polycarbonate, water absorption

INTRODUCTION

Polymer blend is a mixture of two or more polymers which typically possesses the combination of the polymers' properties. Polymer blending is considered as the most versatile and economic way to engineer a material with complex desired properties (Saion *et al.*, 2005; Moldovan *et al.*, 2008; Yousif *et al.*, 2006). Polypropylene (PP) was blended with Polycarbonate (PC) with the prime objective to improve poor impact strength of PP while having sufficient stiffness. Upon the successful effort, research on PP/PC blends has moved beyond impact strength and stiffness, as other properties of the blends were also studied. For instance, thermal properties of PP/PC had been the subject of several studies and improvement in PP thermal stability was reported (Chand and Hashmi, 1999; Renaut *et al.*, 2005). However, characterization data of PP/PC blend is still lacking and issues such as water absorption of the blend needs to be comprehended.

In PP/PC blend, PC is a polar polymer which is susceptible to chemical reaction with polar solvent such as water and oxygen in carbonate group, CO₃, found in PC makes it more prone towards water absorption (Merdas *et al.*, 2002). Besides that, one of the mechanisms for water penetration into polymer composite is governed by capillary action, in which water molecules flow into the interface between matrix and reinforcement. This mechanism is particularly important when the interfacial adhesion between the matrix and reinforcement is weak, especially in the case of polymer blend composite (Kushwaha and Kumar, 2010). Previously, amorphous PC is blended

with semi-crystalline polyethylene terephthalate (PET) to improve solvent and chemical resistance. This is one of the examples of how polymer blending can improve specific properties of a material and produce a more useful and commercially attractive product.

Materials having oxygen or oxy-hydrogen groups are very susceptible to water absorption, whereas plastics containing only hydrogen and carbon, such as polyethylene, polystyrene and PP are extremely water resistant. In addition, PP also provides excellent resistance to organic solvents, degreasing agents and electrolytic attack (Tripathi, 2002). Therefore, blending PP with PC was expected to reduce PC's affinity to water. In summary, this research is aimed to characterize the water absorption properties of PP/PC/PP-g-MA polymer blends. PP-g-MA as compatibilizer has been suspected to improve interfacial adhesion between PP and PC phase (Renaut *et al.*, 2005) and is intended in this work to reduce water absorption caused by capillary action.

Water absorption's threats: Mechanical, physical, chemical and dimensional properties could suffer from detrimental effect because of water/moisture absorption of polymers (Choqueuse *et al.*, 1997; H'ng *et al.*, 2011). Some polymers swell and soften while some even dissolve in water such as nylon and polyvinyl alcohol (Merdas *et al.*, 2002). In the case of swelling and soften, molecular mobility is increased through the absorption of water. By the crowding of solvent molecules, polymer structure will open up and swell, leading to increase in spacing between polymer molecules. This will lower the secondary bonding and result in less resistance to applied stress from the decrease in intermolecular friction, allowing for easier translational motion (White, 2006).

Water absorption in polymers also poses a threat during processing. Even with 0.2% water absorption, polymer could suffer from hydrolytic degradation during melt processing, resulting in significant loss of mechanical and physical properties. Hydrolytic degradation is a chemical reaction which occurs at high temperature with some polymers in the presence of water. It causes primary bonds in the molecular chains to be broken down severely, thus reducing molecular weight. Hence for a hydrophilic polymer such as PC, preparation or pre - treatment before compounding such as drying is a very important step taken to ensure its physical and mechanical properties will not be reduced.

Kinetics of water absorption: Water and moisture penetration into composite materials is governed by four different mechanisms (Karmaker, 1997; Gaudichet-Maurin *et al.*, 2008). The first one is the diffusion of water molecules inside the microgaps or free volume between polymer chains. Next is the capillary transport of water molecules into the space between matrix and reinforcement phase due to the imperfection interfacial bonding between the two phases, especially when they are of different polarities and immiscible with each other. Then, the presence of voids in matrix composite from compounding process that allow for water penetration. Recently, solubility is cited as another mechanism, especially in amorphous polymers of low to moderate hydrophilicity (Gaudichet-Maurin *et al.*, 2008).

Despite of all the water absorption mechanism, many researches (Kushwaha and Kumar, 2010) claimed that the overall effect can be conveniently modeled by using only the diffusion mechanism. Diffusion mechanism can be divided into three cases according to Eq. 1 (Kushwaha and Kumar, 2010):

$$\frac{M_t}{M_s} = kt^n \quad (1)$$

where, M_t is the composite's moisture content at time t , M_s is the moisture content at equilibrium, k is a constant of interaction between the composite and water and n is a constant which indicates the diffusion case. The value of $n = 0.5$ when the diffusion follows Fick's law (case 1), $n = 1$ when the moisture equilibrium in the composite is rapidly reached and maintained with increasing time (case 2) and n value in between 0.5 and 1 for the anomalous diffusion (case 3).

Most of the time, Fick's law will govern the process in water absorption of polymer composite. In this case, when plotted in a graph, the mass of absorbed water increases linearly with square root of time, then the rate slowly decreases until equilibrium plateau reached (Dhakal *et al.*, 2007). Fick's law is given by Eq. 2 (Kushwaha and Kumar, 2010):

$$\frac{M_t}{M_s} = \left(\frac{4}{h}\right)\left(\frac{S}{\pi}\right)^{1/2} t^{1/2} \quad (2)$$

where, h is specimen thickness and D is the diffusion coefficient which represents the ability of water molecules to penetrate inside the composites. The higher D value, the higher the value of maximum water absorption. Higher D value also might suggest the presence of high void content in the composite (Kushwaha and Kumar, 2010).

MATERIALS AND METHODS

PP used was Propelinas G425, produced by Polypropylene Malaysia (PETRONAS) and has Melt Volume-flow Rate (MVR) of 11.0 cm³/10 min while PC was from the trade name Panlite[®] grade L-1225Y, manufactured by Teijin Kasei America Inc. (Teijin Chemicals), with MVR value of 11.0 cm³/10 min (300°C/1.2 kg). The compatibilizer selected was PP-g-MA from the brand Sigma-Aldrich, with molecular weight of 9100 by gel permeation chromatography (GPC) and maleic anhydride content of 8-10%.

Sample fabrication: PC was dried at 95°C for 12 h prior to compounding to minimize hydrolytic degradation. Pellets of PP, PC and PP-g-MA were mixed according to designated weight fractions. The blends, containing between 0-35% of PC and 5% compatibilizer were compounded by twin-screw extruder at 250°C and 100 rpm before formed into standard shapes by compression molding, with temperature ranging from 190-250°C.

Microscopy: Scanning Electron Microscope (SEM) was used to study the morphology of the blends. Specimens were cryogenically fractured and plated with thin gold layer as preparation.

Water absorption test: Water absorption test was done according to ASTM D570. Specimens were molded in the shape of cylinder with 50.8 mm diameter and 3.2 mm thick and for each blend composition three specimens were produced. The picture of the specimens is presented in Fig. 1. Before immersion, the specimens were conditioned by drying in an oven for 24 h at 50°C, cooled in desiccators and immediately weighed to the nearest 0.0001 g. The immersion took place in distilled water at 23°C and after 24 h, they were taken out from the distilled water, wiped with dry cloth and weighed to the nearest 0.0001 g. Upon weighing, the specimens were immersed again in distilled water and re-weighed again after 7 days. After that, the weighing were done per two-week period and halted once the weight increase was less than 5 mg, shown by three consecutive weighing. Finally, the samples were dried in an oven for 3 days at 50±3°C and then weighed again.

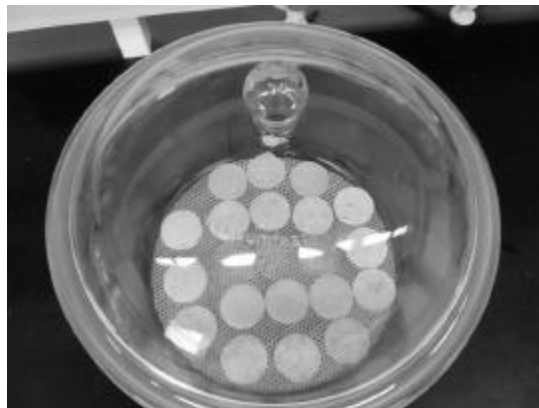


Fig. 1: Water absorption specimens cooled in desiccators

Data after the drying are called the corrected values. This was done to cater the effect of samples dissolution, if any occurred. Similar steps were repeated for immersion at 100°C.

RESULTS AND DISCUSSION

Water absorption: The results of water absorption at 23°C are shown in Fig. 2. The water absorption value, M percentage, is expressed in wt.% and calculated by Eq. 3:

$$\text{M percentage (wt.\%)} = \frac{M_u - M_d}{M_d} \times 100 \quad (3)$$

with M_u is the wet weight of specimen while M_d is the initial weight of dry specimen. The results in Fig. 2a show that all the samples exhibited the same pattern. Rate of absorption is high at the beginning, then slowly decreasing and finally remains relatively constant. When it becomes constant, the sample is regarded as substantially saturated. The absorption summary is tabulated in Table 1. When Fick's diffusion behavior is plotted in a graph, the mass of absorbed water increases linearly with square root of time, then slowly the rate decreases until equilibrium plateau is reached (Dhakal *et al.*, 2007), as can be observed in Fig. 2b.

Generally, it can be observed that as PC content increases, water absorption also increases. PC and water are polar polymer and polar solvent, respectively. Therefore, solvent-solute interaction, namely "like dissolves like" will occur. PC also contains oxygen in carbonate group, CO_3 which is susceptible to water absorption. Crowding of water molecules at PC polymer chain causes the polymer structure to deform and open up, leading to higher free volume (White, 2006). With higher free volume, more water could penetrate in and this is the reason PC has the highest water absorption value. Increasing PC content in PP/PC/PP-g-MA blends will cause the blends to have polar charge, hence increasing its water absorption.

Besides the normal diffusion mechanism, it is suspected that capillary transport of water molecules into the space between PP matrix and PC reinforcement phase potentially occurred. This absorption mechanism is important, especially when interfacial adhesion is weak (Kushwaha and Kumar, 2010). This is due to the imperfection interfacial bonding between the two phases since they are of different polarities and immiscible with each other (Karmaker, 1997).

The highest level of absorption among the blends was 0.260 wt.% which is still considered as small. Therefore, it can be deduced that the interfacial adhesion between PP matrix to PC

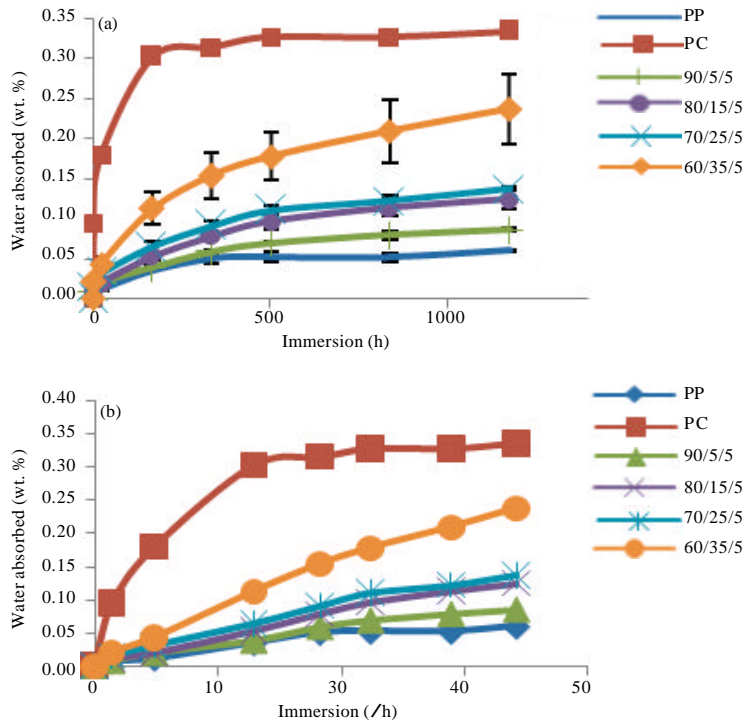


Fig. 2(a-b): Plot of water absorption at 23°C versus, (a) Immersion time and (b) Immersion time square root

Table 1: Water absorption value at 23°C immersion

Blends	Water absorbed (wt.%)	
	1176 h	Corrected
PP	0.060	0.064
PC	0.335	0.362
90/5/5	0.086	0.095
80/15/5	0.125	0.141
70/25/5	0.138	0.151
60/35/5	0.238	0.260

reinforcement is higher than the polar bonding of the water molecules. Otherwise, the water absorption level could have been higher.

Results of immersion in 100°C distilled water for 168 h are shown in Fig. 3. After samples drying in oven for 3 days at 50±3°C, corrected values were determined. The immersion data and corrected values are tabulated in Table 2. Except for 60/35/5, all the other blends showed reduction in water absorption level compared to pure PP. Similar to the previous result of water immersion at 23°C, as PC content increases in the blends, the water absorption also becomes greater. The trend of blends showing lower absorption value compared to PP at elevated temperature can be traced back to the blends improved thermal stability.

Fick's diffusion Eq. 1 is used for analysis purpose. From the equation, the agreement towards Fick's law is governed by n value. To determine the value of n, Eq. 1 was modified into Eq. 4 (Kushwaha and Kumar, 2010):

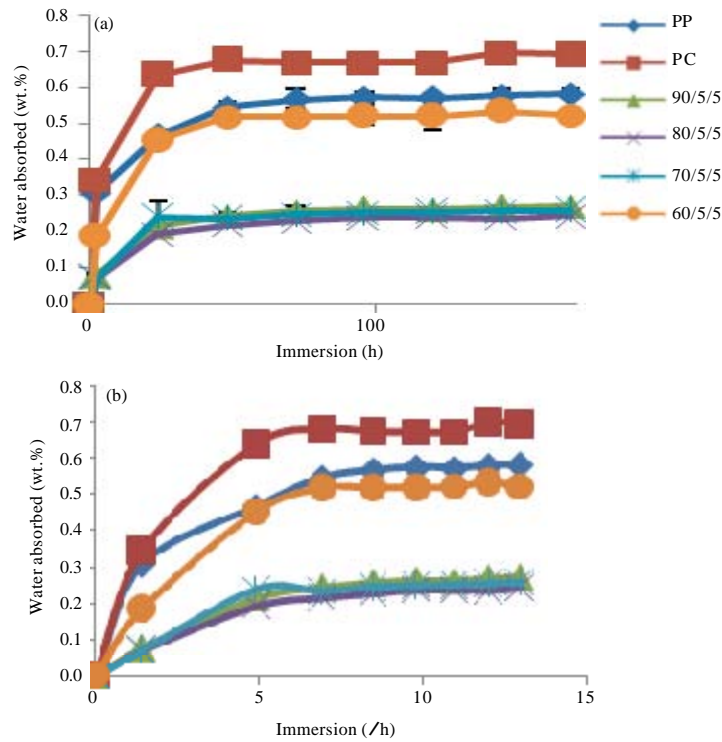


Fig. 3(a-b): Plot of water absorption at 100°C versus, (a) Immersion time and (b) Immersion time square root

Table 2: Water absorption value at 100°C immersion

Blends	Water absorbed (wt.%)	
	168 h	Corrected
PP	0.581	0.571
PC	0.691	0.701
90/5/5	0.271	0.345
80/15/5	0.243	0.348
70/25/5	0.259	0.372
60/35/5	0.595	0.452

$$\log\left(\frac{M_t}{M_s}\right) = \log(k) + n \log(t) \quad (4)$$

Figure 4 shows an example of fitting experimental data according to Eq. 4. The values of parameter n obtained from curve fitting are summarized in Table 3. It can be observed that the values of n for immersion at 23°C are ranging from 0.205-0.403. They are below 0.5 which is the value of n for when the diffusion follows Fick’s law. The closer n value to 0.5, the more water diffusion follows Fick’s diffusion law. In the meanwhile, immersion in 100°C distilled water also shows the same trend, where the values of n are still lower than 0.5. However, the n values are lower than that of 23°C immersion. The range of n values is 0.148-0.283.

According to Fick’s law, the ability of water molecules to penetrate inside a composite can be represented by diffusion coefficient, D. The diffusion property was obtained by determine the first

Table 3: Summary of n values for immersion at 23 and 100°C

Blends	n-value	
	23°C	100°C
PP	0.364	0.148
PC	0.205	0.154
90/5/5	0.386	0.283
80/15/5	0.403	0.277
70/25/5	0.354	0.281
60/35/5	0.397	0.235

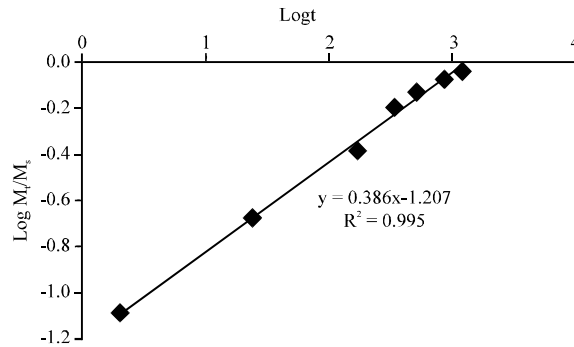


Fig. 4: Fitting of experimental data to find n value for 90/5/5 composition at 23°C

slope of water absorption (in wt.%) curve versus square root of time, then D was calculated using Eq. 5 (Dhakal *et al.*, 2007):

$$D = \pi \left(\frac{kh}{4M_s} \right)^2 \tag{5}$$

where, k is the initial slope of water absorption weight gain versus square root of time, h is the thickness of specimen which is 3.2 mm in this case and finally M_s is the equilibrium water absorption value.

The values of D are summarized in the Table 4. The higher D value, the higher the value of maximum water absorption will be. For immersion at 23°C, generally the D values for PP/PC/PP-g-MA blends are showing increment as PC content increases, except for 60/35/5 composition. This is in agreement with the actual result of their water absorption, where higher PC content will lead to higher water absorption. For immersion at 100°C, the values of D are no longer showing correlation with the water absorption of the blends. This is because water absorption kinetics of the blends in 100°C is deviating quite far from the ideal Fick’s diffusion law. It also suggests some other mechanism of absorption occurred apart from diffusion.

When comparing the effect of temperature towards water absorption, it can be concluded that at 100°C the absorption value is much higher than that of 23°C. The same trend occurs for diffusion coefficient, D, value. This suggests that different sorption kinetics took place when the samples were immersed in 100°C, compared to 23°C. The high and fast water absorption may be attributed to degradation in the matrix - reinforcement interface region, caused by moisture and elevated temperature. After the degradation, the damage in the matrix-reinforcement phase makes the water transport mechanism even more active (Comyn and Marom, 1985).

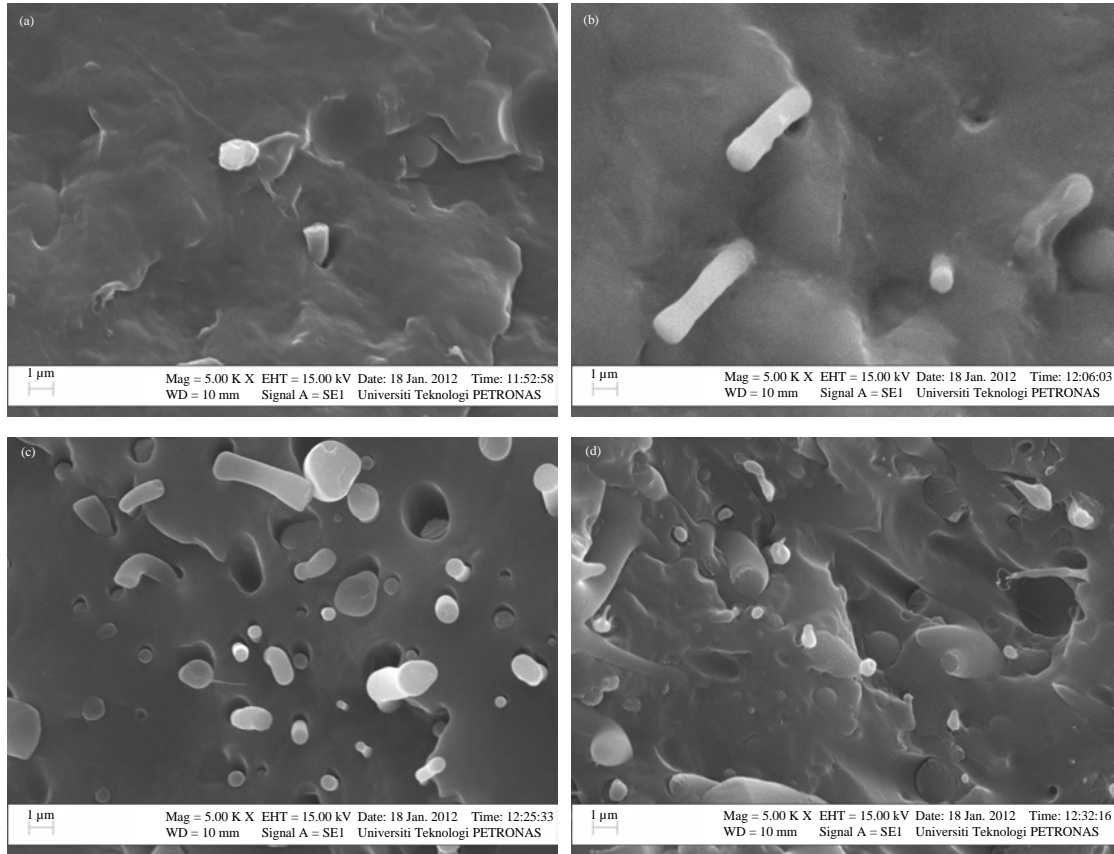


Fig. 5(a-d): The 5000x magnification of PP/PC/PP-g-MA (a) 90/5/5, (b) 80/15/5, (c) 70/25/5 and (d) 60/35/5 by SEM

Table 4: Summary of diffusion coefficient (D) values for immersion at 23 and 100°C

Blends	D (mm ² h ⁻¹)	
	23°C	100°C
PP	0.01227	0.29005
PC	0.06692	0.23940
90/5/5	0.00559	0.04933
80/15/5	0.00645	0.04142
70/25/5	0.00878	0.03640
60/35/5	0.00585	0.09751

Table 5: Results of PC fibers' diameter from SEM

Blends	90/5/5	80/15/5	70/25/5	60/35/5
PC fibers' diameter (μm)	1.005	0.947	0.514	0.452
	-1.160	-1.800	-2.190	-1.390
Diameter range (μm)	0.155	0.853	1.676	0.938

Morphology: SEM was used to observe the morphology of compression molded samples. The micrographs are shown in Fig. 5 while PC fibers' diameter results are tabulated in Table 5.

The morphologies show that PC existed as fibers, dispersed throughout PP matrix. Generally, as PC content in compatibilized blend increases, the fibers' diameter range also increases. This is true except for 60/35/5 composition that exhibited the smallest range among the compatibilized blends. It is suspected that as PC amount increases, the chances for PC fibers to coalesce with each other increases, thus bigger fiber diameter will be produced.

CONCLUSION

Except for 60/35/5 composition, all other blends showed lower water absorption than pure PP when immersed in 100°C distilled water. The reduction of water absorption compared to pure PP was up to 39.6%, showed by 90/5/5 composition. The improvement in the thermal stability of the blends was proven to be beneficial in accelerated aging of water immersion. In the meanwhile, immersion at 23°C demonstrated that PP/PC/PP-g-MA blends were having water absorption values in between PP and PC. As PC content was increases, water absorption becomes greater. In general, water absorption at 23°C is still considered low, despite the weak interfacial adhesion of the blends that can cause high water absorption.

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